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COMPOSITION FOR USE IN A DISHWASHER

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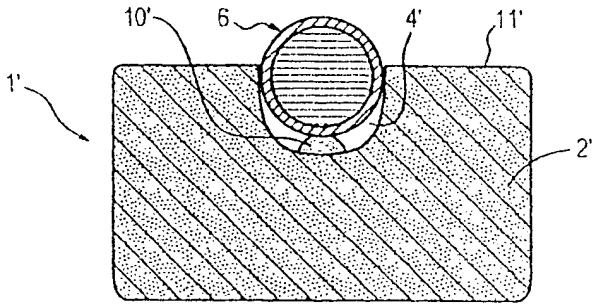
Abstract

The invention relates to a composition for use in a dishwasher which is provided in the form of a tablet. The inventive composition is characterized by a base composition which essentially carries out its function during the main cleaning cycle of the dishwasher, and is also characterized by at least one particle. Said particle has at least one core that comprises at least one substance which essentially carries out its function during the rinse cycle of the dishwasher. The particle also has a coating which, for the most part, completely surrounds the core(s). Said coating comprises at least one compound whose solubility increases with a declining concentration of a specific ion in the surrounding medium. The at least one particle is arranged in or on the tablet in such a way that the surface of the particle(s) is, at most, partially in direct contact with the surface of the base composition surrounding this/these particles. In order to prevent the coating from substantially dissolving or to prevent the coating from substantially detaching from the core(s), the concentration of the specific ion in the local surrounding of the particle(s) is sufficiently high until the tablet has, for the most part, completely dissolved. The invention also relates to a method for conducting a dishwashing cycle in a dishwasher while using the inventive composition.



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This invention concerns a composition for use in a dishwashing machine and a method for its use.

Although modern dishwashing machines in most cases have a large number of different wash programs which differ in the length and temperature of the individual wash cycles, all wash programs essentially consist of the following basic steps: a prerinse cycle; main wash cycles; one or more intermediate rinse cycles; a clear rinse cycle; and drying. While the actual machine dishwashing agent, which is supposed to produce the cleaning action, is added at the beginning of the main wash cycle, special agents are used in the clear rinse cycle, for example clear rinses. As dishes are rinsed with water, clear rinses are supposed to prevent water drops, which leave spots of substances/salts dissolved/dispersed in the drops after drying, from remaining on the rinsed dishes.

These two functionalities, namely the washing action of the machine dishwashing agent on the one hand and the described function of a clear rinse agent on the other, have been achieved up to now by means of two products dispensed with separate dispensing devices and at different times in the dishwashing cycle.

Besides the use of clear rinse agents, there is still the need for other substances that can develop their activity in the rinse cycle, such as an antibacterial activity (for example, cationic compounds or Triclosan), antitarnish agents for silver (for example, benzotriazole), addition of fragrance (fragrances, perfume), bleaching action/disinfection (for example, chlorine bleaches), odor masking (for example polyvinylpyrrolidone), antideposition agents and enzymes for additional purposes (for example, lipase for removal of fat deposits in the dishwasher). However, today's dishwashers do not have dispensing systems available that are suitable for this.

The goal of this invention was to combine in one product the washing function and the function(s) of the substance(s) added in the clear rinse cycle while maintaining as much as possible the performance that can be achieved with separate dispensing, or to enable the dispensing of substances other than the clear rinse agent in the clear rinse cycle.

Molded detergents for use as laundry detergents are known from the German Patent Applications (Offenlegungsschrift) 20 65 153 and 20 07 413, where among other things it is proposed to combine two components with different functionalities. Here a structure is proposed consisting of a casing shell that is composed, for example, of two shell halves that consist of a cleaning agent, and a hollow space enclosed by the shells which contains additives like softeners, bleaches, etc.

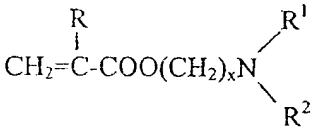
British Patent 1 390 503 discloses a liquid detergent that contains capsules that are insoluble in the composition, but that release their contents when the composition is diluted with water. This goal is achieved by the fact that the capsules are coated with a substance that has poor solubility in water solutions with high ion strengths, but becomes soluble when the ion

strength is lowered through dilution. It is pointed out that this technique can be used to incorporate into the liquid cleaning agent materials that are unstable in the liquid cleaning agent itself or that would produce an instability if they were added directly. The use of this technique to delay the release of a specific substance is also proposed. The use in machine dishwashing agents is claimed and is proposed for encapsulation of tribromosalicylanilide in order to stabilize it. The encapsulated material is released within 2 min after diluting the washing agent with water, i.e., already in the main wash cycle.

US Patent 4,082,678 describes a fabric conditioning product that consists of a closable container that contains a releasable agent that serves to make an inner container that is normally water-soluble or water-dispersible insoluble or nondispersible in water, where the inner container, which is arranged in the main container, contains a fabric conditioning agent. The inner container consists of a substance whose solubility in water is highly dependent on the ion strength or the pH of the surrounding medium, and the agent that serves to make the inner container insoluble is an agent for controlling the pH or the ion strength.

The Japanese Kokai Patent Application Nos. 60-141705, 61-28440, 61-28441, 61-28596, 61-28597 and 61-28598 describe methods for producing pH-sensitive microcapsules for use in laundry detergents. The pH-sensitive coating is a copolymer of the following monomers:

A) at least one basic monomer of formula I:



(I)

in which R is hydrogen or a methyl group, R^1 and R^2 are each an alkyl group with 1-3 carbon atoms and x is a whole number from 1-4;

B) at least one monomer that is insoluble or poorly soluble in water; and

C) at least one water-soluble monomer.

It is indicated that the described polymers are insoluble at a pH of 9.5 or higher and become soluble at a pH of 8.5 or lower. Various components of cleaning agent compositions that can be coated successfully and usefully by the described polymers are described. The goal of the invention described there is to protect substances that are not supposed to develop their function until the rinse cycle begins and then to release them as promptly as possible. The use for dishwashing machines is not described.

A disadvantage of the solution described in these Japanese patent applications is that the coated particles are in direct contact with nonalkaline wash water at the beginning of the wash cycle, which can have dissolution of the protective coating as a consequence.

A laundry auxiliary agent that is surrounded by a water-soluble coating that is obtained by mixing polyvinylacetaldialkylaminoacetate and at least one organic acid that is solid at room temperature is known from Japanese Kokai Patent Application No. 50-77406. This protective coating is supposed to protect the laundry auxiliary during the main wash cycle and release it during the rinse cycles. The described compound reacts to the change of the pH between the main wash cycle and the rinse cycles. The correspondingly coated particles are mixed with conventional powdered laundry detergent. Here, too, there is the disadvantage of possible dissolution of the protective coating at the beginning of the wash cycle.

A water-soluble polymer film for release of wash additives in the rinse cycle of washing machines that remains intact during the normal wash cycle over a range of typical temperatures and rapidly dissolves in the rinse cycle is known from European Patent Applications EP 0 284 191 A2 and 0 284 334 A2. It is pointed out in these applications that the use of pH-sensitive coatings is already known, but these films are normally also temperature-sensitive, so that they are not reliably stable at various temperatures in the wash cycle. It is proposed as a solution to combine a pH-dependent material (which undesirably also shows a positive temperature-dependent dissolving behavior) with a material that has a negative temperature-dependent dissolving behavior. This combination is supposed to guarantee that the coatings do not dissolve at the high temperatures at the beginning of the wash cycle (especially the very high temperatures that occur in American machines). A use for machining dishwashing agents is not claimed.

European Patent Application EP 0 481 547 A1 discloses multilayer machine dishwashing agent tablets with a core, a separating layer surrounding the core, and an outer layer for sequential release of the ingredients of the different layers. Basically, two tasks are supposed to be solved with these tablets, namely 1) incompatible materials can be formulated together in a single tablet and released at different times in order to avoid a mutual influence on each other; and 2) compositions that are supposed to develop their functions at different times can be formulated in a single tablet.

A disadvantage of the prior art described in this publication lies in the fact that the successive molding of the individual components is described as a single production process. Because of this, there is the danger that the core and/or the coating of the core will be deformed, which on the one hand leads to damage (and thus a reduction of the protective effect) of the coating of the core, and, on the other hand (in each case according to the composition of the core), to "bleeding" of the core into the material of the coating and the base composition. Moreover, intimate full-surface contact between the individual layers can result in undesirable reactions occurring in the boundary layers, especially between the coating and the base composition.

A second important disadvantage of this prior art lies in the fact that the temperature and/or, in particular, the contact time with the wash solution is utilized as a triggering factor to initiate the dissolution of the coating layer, i.e., temperature-sensitive materials are used for the material of the coating. Since the temperature/time pattern in dishwashing machines can vary significantly according to the selected program, it is difficult, if not impossible, to choose a material for the coating that can be used for all possible programs of modern dishwashing machines. EP 0 481 547 A1 itself concedes (page 7, lines 37-43) that the choice of the material of the coating layer must take into account peculiarities that are specific to the machine and program. The practical usefulness of the described products is clearly limited for this reason.

PCT Application WO 95/29982 discloses a machine dishwashing agent with delayed release of a clear rinse agent in the form of a nonionic surfactant, where this nonionic surfactant, together with an inorganic builder salt, forms a core particle that is provided with a waxy coating in order to guarantee the delayed release. This coating is a substance that does not melt at the operating temperatures that occur in the cleaning cycle, but is gradually chemically disintegrated at an alkaline pH, so that an effective amount of the clear rinse agent still remains in an excess amount at the end of the main wash cycle and is carried over into the clear rinse cycle.

In this, it is disadvantageous that the coating is made soluble by chemical saponification at an alkaline pH, so that the time at which the clear rinse substance is released from the core is a function both of the temperature and of the length of the main wash cycle. The patent application does not contain any teaching of how to formulate a product with which the clear rinse agent is not released until the clear rinse cycle in every wash program of any type of machine. Moreover, the component of the core that is active as clear rinse agent is a nonionic surfactant, which is absorbed on an inorganic builder salt. This produces inferior clear rinse results, especially the formation of spots on glass. Finally, the product is a mixture of the granular washing agent and granular clear rinse particles.

This invention, in view of the stated prior art, is based on the task of developing a generic composition that is usable for most dishwashing programs of various types of dishwashing machines and in each one of these instances, the substance(s) that is (are) not supposed to develop its effect essentially until the clear rinse cycle, is also not released until the start of the clear rinse cycle at the earliest. Here the aim is to achieve this without any extensive restriction in the choice of the washing agent that is used, the substance(s) that is (are) used for the clear rinse cycle, or other ingredients of the composition.

In accordance with the invention, this task is solved with a generic composition that is characterized by a base composition in the form of a tablet that develops its function essentially in the main wash cycle of the dishwashing machine; and at least one particle with at least one core that consists of at least one substance that develops its function essentially in the clear rinse

cycle of the dishwashing machine, and a coating essentially completely surrounding the core(s), which consists of a compound whose solubility decreases with decreasing concentration of a specific ion in the surrounding medium; where the at least one particle is arranged in or on the tablet so that the surface of the particle(s) is at most partially in direct contact with the surface of this (these) surrounding base composition(s), and the concentration of the specific ion in the local vicinity of the particle(s), until the tablet has essentially completely dissolved, is high enough in order to prevent significant dissolution of the coating or significant separation of the coating from the core(s).

It is preferably provided that the particle or all of the particles is/are held in at least one hollow space of the tablet that is completely surrounded by the base composition and that has a larger volume than the particle or all of the particles that is/are held in the relevant hollow space.

Here the particle(s) in one alternative can be loosely arranged inside the hollow space or, in another alternative, can be fixed in it. If the particles are fixed in the hollow space, this preferably takes place by means of an adhesive.

In a particularly preferred embodiment of the invention, the hollow space is essentially arranged centrally within the tablet.

The invention additionally calls for the tablet to have a single essentially spherical hollow space in which is preferably held a single essentially spherical particle, whose outside diameter is less than the inside diameter of the hollow space.

In an alternative embodiment of the invention, it can be provided that the particle or all of the particles is/are held in at least one hollow space of the tablet, which [hollow space] is only partially surrounded by the base composition.

Here the hollow space is preferably a recess in one of the surfaces of the tablet, in which the particle(s) is (are) at least partially held.

Here the particle(s) is (are) preferably held in the hollow space or in the recess so that it (they) does (do) not project above the surface(s) of the tablet.

It is provided in one embodiment of the invention that the hollow space or the recess has an essentially circular cross section parallel to one of the surfaces to which it opens or in which it is arranged.

The invention proposes in one particular embodiment that the hollow space or the recess be open to the surface(s) only to an extent such that the particle(s) held therein cannot pass through the opening(s) of the hollow space or the recess.

Here it is provided that the particle(s) are loosely arranged in the hollow space or in the recess.

However, it can also be provided that the particle(s) are fixed in the hollow space or in the recess, where this fixing can preferably take place with an adhesive.

The invention preferably provides for the base composition to consist of at least one composition that is chosen from the group that consists of a machine dishwashing composition, a water softening composition and a wash booster composition.

The invention preferably provides that the coating consists of at least one compound that is not or is only slightly soluble at the concentration of the specific ion at the end of the main wash cycle of the dishwashing machine and exhibits, at the concentration of the specific ion in the clear rinse cycle, solubility sufficient that it dissolves or separates from the core(s) in the clear rinse cycle to the extent that an at least partial escape of the core material into the medium of the clear rinse cycle becomes possible.

Here it is preferably provided that the solubility of the compound decreases with decreasing OH^- ion concentration and thus decreasing pH in the surrounding medium.

In a particularly preferred embodiment, the invention proposes that the compound show no or only slight solubility at a pH above 10 and solubility at a pH under 9 sufficient that it largely dissolves or is separated from the core(s) in the clear rinse cycle so that at least partial escape of the core material into the medium of the clear rinse cycle becomes possible.

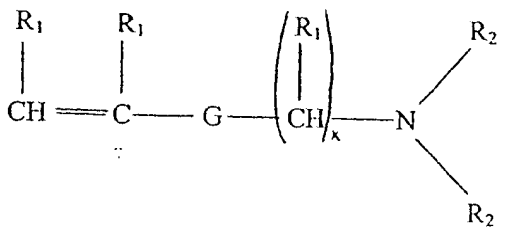
Preferably, this compound consists of a polymer, especially preferably a pH-sensitive polymer, that consists of at least one repeating unit that has at least one basic function that is not a part of the backbone of the polymer.

In a preferred embodiment, the polymer consists of at least one repeating unit is derived from a compound chosen from the group that consists of vinyl alcohol derivatives, acrylates or alkyl acrylates that have said basic function.

In a particular embodiment of the invention, the polymer is a carbohydrate that is functionalized with said basic function.

Said basic function is preferably an amine, especially preferably a secondary or tertiary amine.

In one alternative, the repeating unit is derived from a compound with the following formula III:

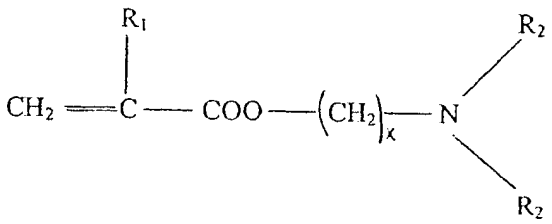


(III)

where G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, -NHCOO-, -OCONH- or -OCOO-, R_1, independent of one another, represent hydrogen or an

alkyl group with 1-3 carbon atoms, R_2, independent of one another, represent hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1 to 6.

Preferably, the repeating unit is derived from a compound with the following formula IV:



(IV)

where R_1, independent of one another, is hydrogen or an alkyl group with 1-3 carbon atoms, R_2, independent of one another, is hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1 to 6.

In further embodiments of the invention, it is provided that the basic function is an imine or a basic aromatic N-containing group, preferably a pyridine group or an imidazole group.

In another embodiment, it is provided that the pH-sensitive polymer is a polymer is derived from chitosan.

Finally, the invention proposes that the compound consists of κ-carrageenan.

In one embodiment of the invention, it is provided that the core(s) consist(s) of at least one material that is selected from the group consisting of surfactants, antibacterial compositions, antitarnish agents for silver, fragrances, bleaches, disinfectants, agents to mask odors, antideposition agents and enzymes.

In an alternative, the core or at least a part of the cores can be in the form of an encapsulated liquid, for example in the form of a liquid contained in a gelatin capsule.

In an alternative embodiment, the core or at least a part of the cores is in a solid form and preferably has a melting point higher than 35°C, especially preferably between 55 and 70°C.

The invention additionally concerns a method for conducting a dishwashing cycle in a dishwashing machine, in which the composition in accordance with the invention is added to the medium in the dishwashing machine at a certain time point during the prerinse cycle or the main wash cycle.

It is provided in a particular embodiment of this method that for the case that the base composition in the form of a tablet is not capable, after it has dissolved in the medium, of making available before the end of the main wash cycle a concentration of the specific ion in the medium that is sufficiently high to prevent significant dissolution of the coating and significant separation of the coating from the core(s), this sufficient concentration of the specific ion is made available

through the addition of an additional composition, for example a machine dishwashing composition, to the medium of the primary wash cycle at a suitable point in time.

The composition in accordance with the invention is characterized by the fact that it affords excellent results both in the main wash cycle and also in the clear rinse cycle of a dishwashing machine. The tablet becomes dissolved during the main wash cycle and can develop its correspondingly intended effect (cleaning, water softening, wash enhancement, etc.). The particles arranged in or on the tablet contain as core material that substance or those substances that is/are intended to develop their primary function in the clear rinse cycle of the dishwashing machine, for example, clear rinse agents.

This/these substance(s) is/are protected by a coating that is stable and does not or only insignificantly dissolves or separates at the ion concentration, for example the pH, and the temperature of the main wash cycle. Only when the ion concentration, or the pH, decreases significantly due to dilution, i.e., at the beginning of the clear rinse cycle, does the solubility of the coating material decrease [sic] so significantly that it dissolves or separates rapidly and releases the actual effective core material into the surrounding medium.

If dispensing via special dispensing means that can hold back the particles in accordance with the invention is not provided, the particles in accordance with the invention should be chosen to be large enough that they are not carried out of the dishwashing machine, at least not to a significant extent, during pumping out after the main wash cycle and the intermediate rinse cycle or intermediate rinse cycles.

It is important for the solution in accordance with the invention that the surface of the particle be at most partially in direct contact with the surface of the base composition of the tablet that surrounds it. This can take place in the manner specifically described and presented in this application, but it can also be achieved in any other way with the desired purpose. Examples are the loose arrangement of a smaller particle in a larger hollow space and the fixing of a smaller particle in a larger hollow space so that there is no or is only partial contact between the particle and the base composition of the tablet, etc.

This constellation [sic] offers the advantage over the prior art that, in the manufacturing process, i.e., in the molding of the individual components that takes place in successive steps, a molding and possibly consequential damage to the core(s) and/or the coating that could occur because of the reduction of the protective action of the coating of the core(s) are reliably avoided. By preventing the exertion of pressure on the particle in any phase of the production process, it is also reliably possible to prevent, for a certain composition of the core(s), "bleeding" of the core into the material of the coating and the base composition. Finally, for specific compositions of the coating or the base composition, it can be advantageous to avoid an intimate full surface contact, since undesirable reactions could arise in the boundary layers.

The term "local environment," as used in connection with the particle in accordance with the invention, is intended to designate the immediate environment around the particle. The ion concentration in this local environment of the particle is the determining factor for its stability. With the products in accordance with the invention, the ion concentration in this local environment is determined, at least up to essentially complete dissolution of the tablet, by the ions that pass from the tablet into solution. Preferably, the origin of the "specific ion" is therefore—at least in the initial phase of the main wash cycle—a compound of the base composition that forms the tablet or is generated by it in the surrounding medium. In the most typical case these are, with the usual basic dishwashing agents, OH^- ions, whose concentration can be expressed as the pH.

If a (for example, basic) machine dishwashing agent composition is not used as the base composition, but rather, for example, a water softener composition or wash booster composition, the protection of the coating of the particle by a sufficiently high ion concentration in the local environment of the particle will possibly be guaranteed only until the tablet is completely dissolved, namely in those cases that the base composition of the tablet is not capable of making available a sufficiently high ion concentration in the medium. In these cases, the sufficiently high ion concentration in the medium (and thus also in the local environment of the particle(s)) will be achieved through the dissolution of the actual machine dishwashing agent (or another special additive).

The invention will now be described in more detail by means of the following examples and drawings. In the drawings:

Figure 1 shows a typical pH profile of a dishwashing machine;

Figure 2 shows a first embodiment of the composition in accordance with the invention in cross section;

Figure 3 shows a second embodiment of the composition in accordance with the invention in cross section;

Figure 4 shows a third embodiment of the composition in accordance with the invention in cross section;

Figures 5a and b show a fourth embodiment of the composition in accordance with the invention in cross section and top view; and

Figure 6 shows a fifth embodiment of the composition in accordance with the invention in cross section.

Basically, the ion concentration or pH profile of the cleaning or washing medium in a dishwashing machine is dependent on the ingredients of the cleaning agent or washing agent that is used. A typical pH profile for using a conventional basic machine dishwashing agent, for example Calognite®, can be found in Figure 1 (dishwasher: Bosch model SMS 3047).

The vertical shaded region shows the time of the following steps: prerinse, main wash, intermediate rinse, clear rinse. It becomes clear that the pH during most of the main wash cycle lies in the range of 10.0-10.5. The pH decreases, after the wash water is pumped out at the end of the main wash cycle and the feed of fresh water, to a value of 9.0 during the intermediate rinse and to a value between 8.5 and 9.0 during the clear rinse.

Figures 2-6 represent possible embodiments of the composition in accordance with the invention.

Figure 2 shows a tablet 1 that consists of two half-tablets 2 and 3, which can have different or the same composition. For example, the conventional commercially sold 2-layer tablet in which both layers usually have a different composition and are differently colored can be used as the foundation.

In both half-tablets, one can see approximately in the middle a roughly hemispherical recess 4 or 5, which, when the tablet 1 is assembled, produces an approximately spherical hollow space.

In this hollow space there is in the embodiment that is shown a single particle 6, which consists of the core 8 and the pH- or ion concentration-sensitive coating 9, whose outside diameter is slightly smaller than the inside diameter of the hollow space in the tablet. Both in the present embodiment, in which the particle is loosely held in the hollow space, as well as in an embodiment where it is fixed in place by adhesive applied in the intermediate space, it is guaranteed that there is not continuous full surface contact between the tablet material and the coating of the particle. This is an important aspect of this invention, in order to prevent, on the one hand, the protective coating around the core of the particle from being damaged during the production cycle and on the other to minimize possible interactions between the tablet material and said coating, both with the goal of keeping the coating reliably stable up to the clear rinse cycle.

To fix the particle in the hollow space, of course, one may consider not only the use of a traditional adhesive, but also other compositions and means that fulfill the same purpose, for example, mechanical securing, such as sufficient frictional engagement between the tablet and particle at at least a few points or a socket connection between the tablet and the particle. Moreover, other connections that melt or dissolve, preferably during the main wash cycle, are possible as securing agents between the particle and the tablet.

Of course, many other geometric shapes are possible for the design of the hollow space in the tablet or the particle held in it, for example ellipsoids, cylinders, etc. The shape and size of the hollow space in the tablet and that of the particle held in it do not have to correspond with each other. For example, a cylindrical particle can be held in a spherical hollow space. All other possible combinations are conceivable within the scope of this invention. In addition, it is

possible to fill the hollow space not just with one particle, but rather with several smaller particles.

Figure 3 shows a second embodiment of the composition in accordance with the invention on a foundation of a conventional 2-layer tablet 1. In this case, the upper half-tablet 3 consists of two parts which make available both a sufficient hollow space 5 for accepting the particle 6 and an opening on the side 11 of the tablet. In this case the particle 6 is not completely surrounded by the base composition of the tablet 1, so that it is externally visible within the tablet 1. The particle can either be loosely held in hollow space 5 (provided it is guaranteed that the particle or particles in the hollow space cannot pass through the opening through the appropriate choice of the size of the particle 6 and the size of the opening of the hollow space 5 turned toward side 11 of the tablet) or it can be fixed within the hollow space 5 by the appropriate means, for example, an adhesive.

A third possible embodiment is shown in Figure 4. The foundation in this case presents a tablet 1', which is uniformly structured, i.e., it consists only of a layer 2' with uniform composition and color. In this layer 2', a recess 4' is formed by means of a suitable device. The particle 6' is placed in this recess 4' and in this case, since the recess is open towards side 11' of tablet 1' so much that it would be possible for the particle to fall out of the recess if it were not fixed in place, for instance, secured in the recess with an adhesive 10' or a fixing intermediate layer or mechanically (for example by frictional engagement). Of course, this principle can also be extended to multilayer tablets.

Many different geometric embodiments are possible in this case as well. For example, the recess can have an essentially circular cross section parallel to side 11'. However, any number of other cross sections is likewise conceivable, for example, any polygon. The particle 6' held in recess 4' can, in this case, as in the embodiment as in Figure 3, take on any shape (and independent of the shape of recess 4'), for example, an ellipsoid, cylinder, cube, etc.

Fixing particle 6' in a hollow space open on both sides in the tablet can also be imagined, for example, a cylindrical hole 4' passing through the tablet body 1', in which a corresponding cylindrical particle 6' is fixed (Figure 5a and b).

Another possible embodiment is shown in Figure 6. This is essentially constructed like the embodiment as in Figure 4, i.e., a tablet 1' which is uniformly formed, i.e., of only one layer 2" with a uniform composition and color. In this case the particle 6", however, contains not only a core (as in Figure 4), but also a number of cores 8", which are all embedded in a coating 9". With this embodiment it is also possible, for example, to incorporate cores of differing composition and differing shape (encapsulated material or solid cores) into a particle 6".

Both with the embodiments shown and with other conceivable alternatives, it is important that a local environment with sufficient ion concentration or pH, which serves as the "trigger" for

dissolving the coating, is present at least in the first phase of the main wash cycle for the particle containing the substances to be released in the clear rinse cycle, i.e., that this environment be present in a phase in which, as is evident from Figure 1, the pH is still relatively low, i.e., it is briefly in a range in which elevated solubility of the coating would result. In this way it is guaranteed that the coating will have sufficient stability until the clear rinse cycle.

Example 1

Preparation of the core

a. Core for a particle for controlled release of a clear rinse agent in the clear rinse cycle

The core(s) of the particle(s) that is (are) supposed to develop its (their) actual activity only in the clear rinse cycle must consist of at least one substance that is effective as a clear rinse agent for this objective. Advantageously, a low-foaming nonionic surfactant is used with this invention. Such surfactants are, for example, fatty alcohol ethoxylates, fatty alcohol ethoxylates/propoxylates, ethoxylate/propoxylate polymers such as the products from the Synperonic® and Brij® series from ICI, the products from the Plurafac®, Pluronic® and Lutensol® series from BASF, the products from the Genapol® series from Clariant and the products from the Polytergent® series from Olin.

Other possible examples of nonionic surfactants are alkyl polyglycosides, glucamides and alkylpyrrolidones. Moreover, of course, all other surfactants that can develop the desired efficacy as clear rinse agents are also possibilities.

Most of the substances known for use as clear rinse agents are liquids or waxy solids. The aggregate state of the substance that is effective as clear rinse agent in any case does not play a crucial role for use in this invention. If liquids are to be used, they can be in the form of surfactant-containing capsules, for example gelatin capsules, or can be converted to a coatable state by other suitable means before application of the coating. Solids can usually be provided with the coating directly, where the coating process possibly has to be matched to the corresponding substance.

For purposes of this invention, melt mixtures that provide solid surfactant particles with a melting point of higher than 35°C, preferably between about 55 and 70°C, have proven to be particularly advantageous.

The combinations of various polyethylene glycols with the surfactant Synperonic® RA 30, a block ethylene oxide/propylene oxide bonded to a C_{13}-C_{15} alcohol, ($C_{13}/C_{15}O(EO)_6(PO)_3$), shown in the following Table 1, were prepared as melt mixtures in the form of cylinders weighing about 0.25 g. The melting point determinations gave the values indicated in Table 1.

Table 1

Code	RA 30 [%]	PEG 8000 [%]	PEG 10000 [%]	PEG 20000 [%]	PEG 350000 [%]	Schmelz-punkt [°C] (1)
C1	30		70			58-63
C2	40		60			57-60
A30	50		50			57-60
A31	60		40			54-58
A30	50	50				57-60
C3	60	40				57-60
C4	65	35				55-59
A33	50			50		59-65
C17	60			40		58-63
C18	70			30		57-64
A34	50				50	59-65
C15	60				40	58-66
C16	70				30	57-64

Key: 1 Melting point (°C)

Although all of the combinations basically can be seen as suitable, the 50:50 mixture A33 in particular showed excellent stability and was easy to handle, especially in view of the subsequent coating processes. All of the samples showed rapid dissolution in water, so that in every case, optimum activity as a clear rinse agent is ensured.

Of course, the invention is in no way limited to the combinations that are presented as examples. Basically speaking, any type of surfactant that can be used as a clear rinse agent is a possibility for use with this invention.

b. Core for a particle for controlled release of a fragrance in a clear rinse cycle

Bleach-containing, i.e., oxidizing, dishwashing agent compositions considerably limit the possibilities for use of fragrances that can be used in such compositions. The controlled release of a fragrance in the clear rinse cycle would enable far greater flexibility in the use of fragrances.

For the controlled release of a fragrance or fragrance composition in the clear rinse cycle, one can produce a core for a particle corresponding to the invention, in which a mixture of 50 wt% molten polyethylene glycol, for example PEG 8000, 25 wt% fragrance or fragrance

composition and 25 wt% diethyl phthalate are chilled in a mold, in order to form, for example, a spherical particle weighing, for example, 0.75 g.

c. Core for a particle for controlled release of an antibacterial composition in the clear rinse cycle

The use of a particle in accordance with the invention with a core or several cores that contain an antibacterial composition in a tablet for use in a dishwashing machine would open up the possibility of simultaneously releasing two different compositions in the clear rinse cycle, namely the antibacterial composition from the core(s) of the particle in accordance with the invention and the clear rinse agent from the usual dispensing device of the dishwasher.

A corresponding core for such a particle is made by cooling a mixture of 100% molten benzalkonium chloride (Barquat®MS-100) in a mold in order to produce, for example, a spherical particle with a weight of, for example, 0.64 g.

d. A core for a particle for controlled release of enzymes in the clear rinse cycle

Since, as is well known, proteases, which are usually used in dishwashing agent compositions, can degrade lipases and thus reduce their activity, it would be desirable to incorporate such lipases into the core(s) of a particle in accordance with the invention, so that the lipases are not released until the clear rinse cycle, which could enable optimum performance for these enzymes.

For this purpose, 0.4 g of a granular lipolytic enzyme (for example, Lipolase® 100T (Novo)) can be put into a hard gelatin capsule with, for example, rounded cylindrical shape, for example, the kind used for drugs.

Example 2

Screening method for coating materials

As noted above, it is of considerable importance for this invention that the material for the coating of the particle core(s), which consist of the substance that develops its function essentially in the clear rinse cycle of the dishwasher, show a solubility that is dependent on the concentration of a specifically selected compound. In this way the coating is essentially insoluble in the main wash cycle and is made soluble and dissolves from the particle when this concentration decreases during the intermediate rinse cycle(s) or the clear rinse cycle.

It was observed that the dilution that occurs in the course of the various wash cycles due to the pumping out of the wash water and the feed of fresh water causes the ion concentration to decrease by 20 to 200-fold between the end of the main wash cycle and the last rinse cycle.

Based on this observation, methods were developed for screening the suitability of various polymers for use as coating materials, which consists of determining the solubility of

such polymers at two different ion concentrations which differ from each other by at least 20-fold, preferably by 200-fold.

The values of the ion concentrations that are supposed to be used in screening the polymers are dependent on the formulation of the base composition of the tablet in which the coated particle is to be incorporated.

In fact, the value for the highest ion concentration that is used for the screening process should correspond to the concentration of the selected ion that is to appear in the wash water after the machine dishwashing agent has dissolved completely. Only after this concentration has first been determined should the lower value for the ion concentration be set to 20-200 times under this higher value.

With these data, it is within the capability and knowledge of one skilled in the art in this field to determine the values for the ion concentration of the test solution that are to be used in the test method described below.

Method for preparing the test solution and carrying out and evaluating the test

The materials to be tested are dissolved in solvents in which they are readily soluble. The solutions are distributed on glass plates and then dried at room temperature until they exhibit constant weight.

The glass plates are put into a beaker containing test solution at a controlled temperature. The solution is then stirred with a magnetic stirrer at a controlled speed. After about 10 min, the glass plates are removed from the beaker and dried to constant weight at room temperature. The results are expressed as weight loss (%).

Of course, the screening method has to match to the composition of the machine dishwashing agent, since this composition has a considerable effect on the ion concentration or pH profile in the dishwasher cycle. The goal in each case is to test the degree of solubility of the corresponding materials under different conditions, namely high(er) or low(er) ion concentrations or pHs.

With this procedure it is merely within the capability of the one skilled in the art in this field to establish particle test parameters for the screening. For example, two screening methods, with which some possible materials for coating the particles in accordance with the invention were tested, are presented in the following.

Screening method 1:

Screening method 1 was carried out with buffer solutions as a medium for simulating the wash water. Two buffer solutions were prepared as follows for this purpose:

Stock solution:

7.507 g glycine buffer (Merck 104169)
5.850 g NaCl
filled with water to 1000 mL

pH 8 buffer solution:

500 mL stock solution
500 mL distilled H_2O
1.23 g 1N NaOH

pH 10 buffer solution:

500 mL stock solution
500 mL distilled H_2O
32.6 g 1N NaOH

Screening method 2:

Screening method 2 was carried out with the following cleaning agent formulation in order to simulate the conditions in various stages of a dishwasher cycle. Concentrations from 4 to 5 g/L are usual for the washing agent load in the wash cycle. Concentrations of about 20-40 mg/L are usual for the clear rinse cycle.

Cleaning agent formulation:

Ingredient	wt%
Sodium perborate monohydrate	9.00
Sodium tripolyphosphate	48.00
Sodium carbonate	28.00
Polyethylene glycol	4.00
Polymer	1.50
TAED	3.00
Enzymes	1.50
Surfactant	3.50
Additives	1.50

Total	100.00

Screening method 3:

Screening method 3 is used to screen for compounds whose solubility changes in dependence on the concentration of potassium ions. The compounds determined with this screening method can be used, when—as previously noted—a correspondingly high concentration of potassium ions that becomes correspondingly reduced in the clear rinse cycle by dilution is present in the main wash cycle.

The screening method 3 was carried out with the following formulation in order to simulate the corresponding conditions.

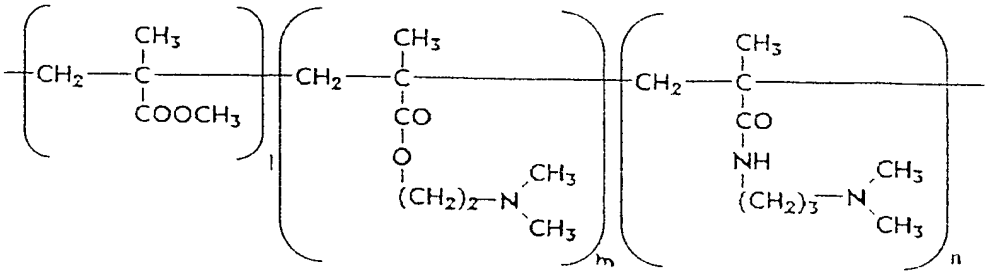
Formulation:

Ingredient	wt%
Potassium tripolyphosphate	13.6
Potassium bicarbonate	34.0
Potassium sulfate	23.1
Potassium chloride	12.4
Potassium carbonate	9.7
Boric acid	2.0
Sodium perborate monohydrate	2.0
TAED	1.0
Paraffin	1.0
Protease	0.2

Example 3

Choice of materials for coating the particles

Various materials were tested for suitability as a coating for particles in accordance with this invention by means of the screening method described in Example 2. One of these materials, "polymer 1" in the following, is a polymer as described in Japanese Kokai Patent Application No. 61-28440, i.e., a polymer of the general formula II with $l/(l + m + n) = 0.35$; $m/(l + m + n) = 0.45$; $l + m + n = 1500\text{-}1800$.



(II)

The polymer was prepared in the usual way by bulk polymerization. The result of the screening tests were as follows:

Screening method 1:

Films of polymer 1 were prepared from a 10% solution in isopropanol.

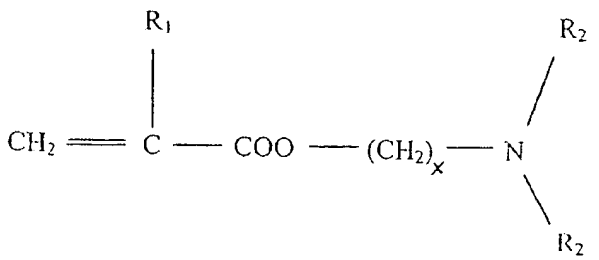
pH of buffer solution	Weight loss at 30°C (%)	Weight loss at 60°C (%)
10	7-8	5-8
8	81-88	91-95

Screening method 2:

Films of polymer 1 were prepared from a 10% solution in a mixture of water and 1N HCl (17:1).

Concentrated washing agent, pH	Weight loss at 30°C (%)	Weight loss at 60°C (%)
4 g/L 10.6	8-15	6-15
0.02 g/L 8.5	90-95	89-95

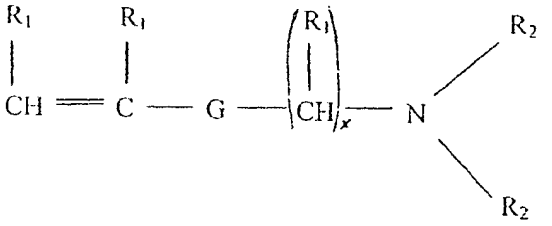
Of course, the invention is not limited to this exemplary polymer, and of course a large possibility for variation already extends to the polymers indicated in the Japanese Kokai Patent Application Nos. 60-141705, 61-28440, 61-28441, 61-28596, 61-28597 and 61-28598, or to compounds of formula IV:



(IV)

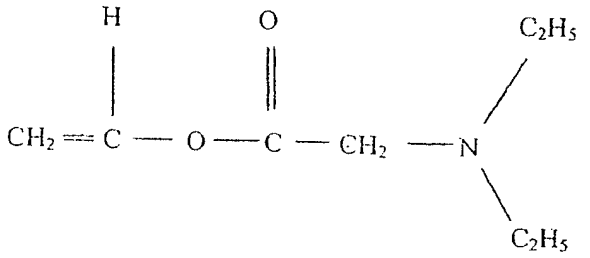
where R_1, independent of one another, means hydrogen or an alkyl group with 1-3 carbon atoms, R_2, independent of one another, means hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1 to 6.

In addition, within the larger class of compounds with formula III:



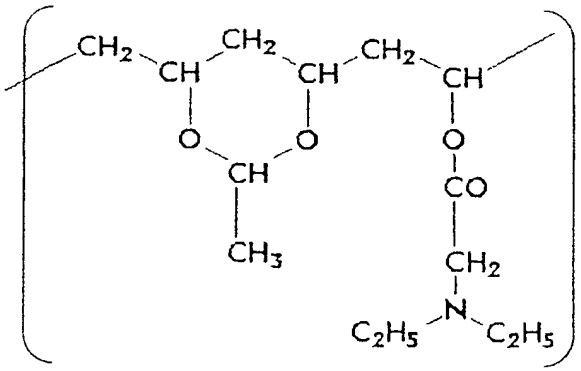
(III)

where G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, -NHCOO-, -OCONH- or -OCOO-, R_1, independent of one another, mean hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1-6, for example, polymers that have a repeating unit is derived from a compound with formula V



(V)

can be used, or a pH-sensitive polymer ("polymer 2") with the repeating unit VI, which is commercially available from the Sankyo Company under the trade name AEA®,



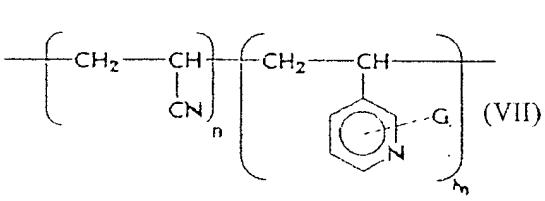
(VI)

The screening method 2 described above was also carried out with "polymer 2":

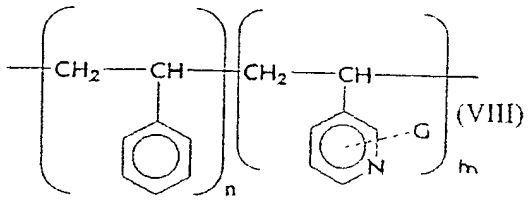
15 g "polymer 2" and 5 g Mowiol® 3-98 (Clariant) were dissolved in 200 mL of a 12:8:1 mixture of water/ethanol/1N HCl. Films were formed and tested as described above. The following results were obtained:

Washing agent concentration pH	Weight loss at 30°C (%)	Weight loss at 60°C (%)
4 g/L 10.6	2-8	5-7
0.02 g/L 8.5	32-40	45-47

Other polymers that show the desired properties or can be modified in a simple way so that they are suitable for the purposes of this invention are polymers of isomers or derivatives of pyridine, preferably copolymers with styrene or acrylonitrile, of the following formulas VII and VIII, in which G represents a substituent at any site on the pyridine ring.



(VII)



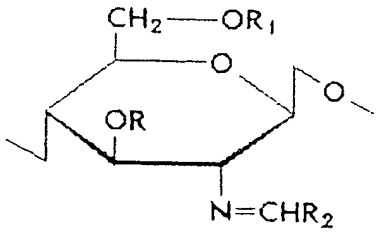
(VIII)

A polymer as in the above formula VIII, namely poly(4-vinylpyridine-styrene) copolymer (Scientific Polymer Products, Inc.), "polymer 3," was tested by the above described screening method 2:

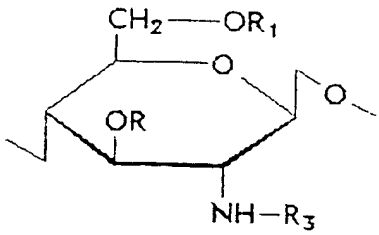
10 g "polymer 3" were dissolved in 230 mL water/1N HCl (6.25:1). Film formation and testing took place as described above. The following results were obtained:

Concentration of washing agent pH	Weight loss at 30°C (%)	Weight loss at 60°C (%)
4 g/L 10.6	0-6	5-12
0.02 g/L 8.5	68-85	92-94

Other polymers are (for example statistical) polymers that are derived from chitosan, on the basis of the following monomer units IX and X



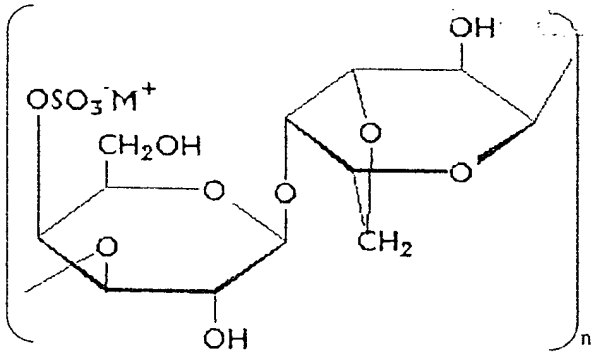
(IX)



(X)

In addition, it is also possible to use substances or substance mixtures in the coating of the core material that react, with regard to their solubility behavior, to a change of the ion concentration, i.e., ion concentration-sensitive polymers. Possibilities here are, for example, the partially hydrolyzed polyvinyl acetates (commercially available under the trade name Mowiol® (Clariant) described in the publications EP 0 284 191 A2 and EP 0 284 334 A2, which show a corresponding ion concentration dependency in the presence of borates, because of complexing between the borates and the polyols. The first successful tests were carried out with the product Mowiol® 56-88.

Another ion concentration-sensitive polymer is the polysaccharide κ-carrageenan, which in screening method 3 (see Example 2) proved to be a polymer that was dependent in its solubility on the calcium ion concentration in the surrounding medium. κ-carrageenan is represented by the following XI:



(XI)

This polymer, designated as "polymer 4," was tested by the above-described screening method 3:

4 g κ-carrageenan were dissolved in 96 g water. 10 g Mowiol® 18-88 were dissolved in 90 g water and the two solutions were mixed together. The resulting solution was used to form films and to carry out the tests, as described above. The following results were obtained:

Concentration of washing agent	Weight loss at 30°C (%)	Weight loss at 60°C (%)
4 g/L	0.5-3.0	11.0-12.0
0.02 g/L	24.5-25.0	78.0-85.0

The above list of compounds that are suitable for the coating in accordance with the invention is, of course, not definitive. Other polymers that alter their solubility in the desired range through changes of the pH or the ion concentration are conceivable or can be developed and thus fall under the extent of protection of this invention. Moreover, the substances suitable for the coating in accordance with the invention are not limited to polymer compounds, even though such compounds are described here as preferred embodiments.

Using the screening methods described above or screening methods matched to the measurement of an ion concentration sensitivity, it is possible to investigate other commercially available materials, or materials obtainable by simple modifications, for their suitability in this invention. The choice of such polymers is a task easily solved by one skilled in the art with the correspondingly clear objective and the given screening methods.

Example 4

Preparation of a particle in accordance with the invention

The various cores described in Example 1 were used as foundations for preparation of the particles in accordance with the invention. These cores individually or severally were provided with a coating in a device for application of a film coating, as is known from the pharmaceutical industry (for example, from the firms Lödige, Hüttlin, GS, Manesty and Driam) (Figure 6).

If the core(s) has (have) an ingredient that shows a certain incompatibility with the material of the coating, it is possible to provide the core(s) with a protective coating before application of this coating. For this, various materials known from the prior art are possibilities, for example, cellulose, cellulose derivatives, polyvinyl alcohol, polyvinyl alcohol derivatives, and mixtures of these. Although it is not absolutely necessary, such a protective coating was used in all cases when using the cores of Example 1, with a 10 wt% aqueous solution of a polyvinyl alcohol or the polyvinyl alcohol Mowiol® 5-88 (Clariant) being preferably used. The amount of the applied protective coating can easily be varied by one skilled in the art in dependence on the composition of the core(s) and can be appropriately adjusted. The first attempts gave good results with 3 wt% of polymer (dry weight), in the case of 1a, 2 wt% in the case of 1b, 3 wt% in the case of 1c and 4 wt% in the case of 1d, in each case with respect to the weight of the total particle.

The ion concentration-sensitive coating can be applied to the core(s) or protective coating basically in any amount and thickness, so long as it is ensured that the coating separates or

dissolves sufficiently rapidly in the clear rinse cycle, so that the substance contained in the core(s) can develop its effect. In a preferred embodiment, 1-10 wt%, preferably 4-8 wt%, of the ion concentration-sensitive coating material (dry weight), with respect to the weight of the total particle, is applied to the cores.

Preferably, the particles in accordance with the invention should have a size such that they are not carried out of the dishwasher, or at least not to a considerable extent, by the pumping operations after the main wash cycle or the intermediate rinse cycle. For this, a size of roughly 1 cm of the largest diameter is usually sufficient. However, smaller or larger sizes can of course be chosen, as long as the function is ensured.

For the further tests, "polymer 1" from Example 3 was used as coating and applied as a 10% solution of the polymer in 0.055N aqueous HCl.

Example 5

Preparation of a 2-layer dishwashing agent tablet with clear rinse particles

A typical 2-layer dishwashing agent tablet that is suitable for holding a clear rinse particle in a hollow space formed in it in accordance with the invention can be produced by molding the powdered ingredients in machines basically known from the prior art and using operating parameters basically known from the prior art. One possible shape of such a tablet is a cubic tablet of two essentially equally thick layers, where a hemispherical recess is formed in the largest surface of each of these layers, so that when the two half-tablets are assembled, an essentially spherical hollow space is formed in it (see Figure 2).

The composition of the dishwashing agent tablet is in this case oriented toward commercial products. An exemplary composition is shown in the following Table 2. Of course, other compositions are also possibilities, especially ones that are optimized to support the compounds surrounding the core, for example, in the making available of alkalinity.

Table 2

	White layer	Colored layer
	50%	50%
Sodium perborate monohydrate	18.00	
Sodium tripolyphosphate	48.00	48.00
Sodium carbonate	245.00	32.00
Polyethylene glycol 6000	3.00	5.00
Polymer		3.00
TAED		6.00
Enzymes		3.00
Dye		0.02
Surfactant	4.50	2.50

Additives	2.50	0.50
	100.00	100.00

Half-tablets weighing about 11.5 g were prepared for the tests conducted in Examples 6 and 7. The hollow space that resulted when the half-tablets were assembled had an inside diameter of about 1.2 cm.

The clear rinse particles prepared in accordance with Examples 1a and 4 are put into the hemispherical recess of the white or colored half-tablet. Then a fixing substance, for example an adhesive (for example, polyethylene glycol, polyvinyl ether, polyvinyl alcohol, silicate, preferably molten PEG 4000) is applied to the corresponding surface of the half-tablet and optionally also to the clear rinse particle, and the second half-tablet (colored or white) is pressed onto the first half-tablet with the clear rinse particle.

Example 6

In this example, a test with which the transfer of the clear rinse surfactant into the clear rinse cycle is observed when using the tablet prepared in accordance with Example 5.

The clear rinse particles have an average content of surfactant or polyethylene glycol of about 0.37 g each. The average amount of water in the clear rinse cycle is about 5.0 L. The maximum amount of surfactant plus PEG to be expected in the clear rinse cycle should therefore be 0.148 g/L when using one tablet per dishwashing cycle.

Three different tests were carried out with three different tablets in a Bosch SMS 3047 dishwasher. The water hardness was about 17° dH.

1. Dishwashing agent tablet without clear rinse particles; temperature 65°C.

2. Dishwashing agent tablet with clear rinse particles (Example 6); temperature 65°C.

3. Dishwashing agent tablet with clear rinse particles (Example 6); temperature 55°C.

With each test, a minimum of 1 L wash water was removed from the clear rinse cycle shortly before the water was allowed to drain. The samples were characterized as 1.1 to 3.3. The water was then analyzed to detect the total amount of surfactant plus polyethylene glycol in the clear rinse cycle. The measurements were carried out by extracting the surfactant and PEG, evaporating the solvent and conducting a gravimetric determination of the nonvolatile residue.

It should be noted that both the nonionic surfactant and the polyethylene glycol are detected with this analysis method.

Table 3

	(1) Versuch 1 mg/l	(n = 1) %	(1) Versuch 2 mg/l	(n = 2) %	(1) Versuch 3 mg/l	(n = 3) %
n.1	1,0		43,6	29,5	91,9	62,1
n.2	10,4		48,8	33,0	64,2	43,4
n.3	7,0		32,7	22,1	76,5	51,7

Key: 1 Test __

Example 7

The test described in this example serves to test the composition in accordance with the invention in view of its efficacy in the clear rinse cycle.

As a comparison with the dishwashing agent tablet prepared in accordance with the invention with clear rinse particles as prepared in Example 6, the clear rinse power of separately added dishwashing agent and clear rinse agent were tested, where the dishwashing agent corresponded to the tablet composition of the tablet in accordance with the invention and a commercial clear rinse agent was used. The dishwasher was a Bosch SMS 3047. The water hardness was about 17-19° dH. The temperature setting was 65°C. The dishwasher was loaded with 20 glasses, 20 black porcelain plates and 20 utensils.

The dishwasher load was soiled as follows:

50 g ground meat (pork: beef, 1:1) was browned with 2 g fat. After a light brownish color had been achieved, a sauce containing 100 mL water, 1 g sauce binder and 2.5 g instant sauce was added to the meat.

This material was put into the dishwasher, and the screen was closed with a stopper in order to keep the soil in the machine until the end of the wash program. The dishwashing agent was dispensed at the beginning of the clear rinse cycle. The evaluation of the dishwasher load was carried out 10 min after the end of the dishwashing cycle.

The visual evaluation followed the following ranking table:

4 points = without any spots

3 points = 1-4 spots

2 points = more than 4 spots to 1/4 of the surface covered by spots

1 point = 1/4 to 1/2 of the surface covered with spots

0 points = almost completely covered with spots.

The spot prevention performance was expressed in percent. 100% performance means the maximum possible point count of 228 points. The results are summarized in the following Table 4:

Table 4

	Performance		
	Cleaning agent + 2 mL clear rinse agent	Cleaning agent + 3 mL clear rinse agent	Tablet with clear rinse agent particles
Porcelain	66.9	75.6	96.9
Glass	25.6	26.9	49.4
Utensils	80.6	90.6	78.8
Total	57.7	64.4	75.0

The results show outstanding clear rinse action for the composition in accordance with the invention. This was particularly pronounced in the case of porcelain and glass, while the performance in the case of utensils was comparable to that of traditional compositions. Surprisingly, there was even, in some cases, a superior clear rinse performance for the composition in accordance with the invention when compared to the traditional procedure of separate dispensing of dishwashing agent and clear rinse agent.

The characteristics of the invention disclosed in this description, the claims, and the drawings can be important, both individually and in any combination, for the attainment of the invention in its various embodiments.

Claims

1. A composition for use in a dishwashing machine, characterized by

- a base composition (2,3;2'), that develops its function essentially in the main wash cycle of the dishwashing machine, in the form of a tablet (1;1'); and

- at least one particle (6;6';6"), with

- at least one core (8;8';8"), that consists of at least one substance that develops its function essentially in the clear rinse cycle of the dishwashing machine, and

- a coating (9;9';9") that essentially completely surrounds the core(s) and that consists of at least one compound whose solubility decreases with a decreasing concentration of a specific ion in the surrounding medium;

where the at least one particle (6;6';6") is arranged in or on the tablet (1;1') so that the surface of the particle(s) (6;6';6") is at most partially in direct contact with the surface of this surrounding base composition (2,3;2') and the concentration of the specific ion in the local environment of the particle(s), up to essentially complete dissolution of the tablet (1;1'), is high enough to prevent significant dissolution of the coating or significant separation of the coating from the core(s).

2. A composition as in Claim 1, characterized by the fact that the particle or all of the particles (6) is/are held in at least one hollow space (4,5) of the tablet (1) that is completely surrounded by the base composition (2,3), which [hollow space] has a greater volume than the particle or all of the particles (6), that is/are held in the relevant hollow space.

3. A composition as in Claim 2, characterized by the fact that the particle(s) (6) is (are) loosely arranged inside the hollow space (4,5).

4. A composition as in Claim 2, characterized by the fact that the particle(s) (6) is (are) fixed in the interior of the hollow space (4,5).

5. A composition as in Claim 4, characterized by the fact that the particle(s) (6) is (are) fixed in the interior of the hollow space (4,5) by an adhesive.

6. A composition as in one of Claims 2-5, characterized by the fact that the hollow space (4,5) is arranged essentially centrally inside the tablet (1).

7. A composition as in one of Claims 2-6, characterized by the fact that tablet (1) has a single essentially spherical hollow space (4,5).

8. A composition as in Claim 7, characterized by the fact that a single essentially spherical particle (6), whose outside diameter is smaller than the inside diameter of the hollow space, is held in the hollow space (4,5).

9. A composition as in Claim 1, characterized by the fact that the particle or all particles (6';6") is/are held in at least one hollow space (4') of the tablet (1') and the hollow space is only partially surrounded by the base composition (2').

10. A composition as in Claim 9, characterized by the fact that the hollow space is a recess (4') in one of the surfaces (11') of the tablet (1') in which the particle(s) (6';6") is (are) at least partially held.

11. A composition as in Claim 9 or 10, characterized by the fact that the particle(s) (6';6") is (are) held in the hollow space or in the recess (4') so that it (they) does (do) not project above the surface(s) (11') of the tablet (1').

12. A composition as in one of Claims 9-11, characterized by the fact that the hollow space or the recess (4') has an essentially circular cross-sectional area parallel to one of the surfaces (11') onto which it opens or in which it is arranged.

13. A composition as in one of Claims 9-12, characterized by the fact that the hollow space or the recess (4') opens toward the surface(s) (11') only to the extent that the particle(s) (6';6") held in it cannot pass through the opening(s) of the hollow space or the recess (4').

14. A composition as in Claim 13, characterized by the fact that the particle(s) (6';6") is (are) loosely arranged in the hollow space or in the recess (4').

15. A composition as in one of Claims 9-13, characterized by the fact that the particle(s) (6';6") is (are) fixed in the hollow space or in the recess (4').

16. A composition as in Claim 15, characterized by the fact that the particle(s) (6';6") is (are) fixed in the hollow space or in the recess (4') with an adhesive (10').

17. A composition as in one of the preceding claims, characterized by the fact that the base composition (2,3;2') consists of at least one composition that is chosen from the group that consists of a machine dishwashing agent composition, a water softening composition, and a wash booster composition.

18. A composition as in one of the preceding claims, characterized by the fact that the coating (9;9';9") consists of at least one compound that is not or is only slightly soluble at the concentration of the specific ion at the end of the main wash cycle of the dishwashing machine, and, at the concentration of the specific ion in the clear rinse cycle, has a solubility sufficient that it is dissolved or separated from the core(s) in the clear rinse cycle to the extent that at least partial escape of the core material into the medium of the clear rinse cycle becomes possible.

19. A composition as in Claim 18, characterized by the fact that the solubility of the compound decreases with decreasing OH^- ion concentration and thus decreasing pH in the surrounding medium.

20. A composition as in Claim 19, characterized by the fact that the compound shows no or only slight solubility at a pH above 10 and shows sufficient solubility at a pH under 9 so that, in the clear rinse cycle, it dissolves or separates from the core(s) to the extent that at least partial escape of the core material into the medium of the clear rinse cycle becomes possible.

21. A composition as in one of Claims 18-20, characterized by the fact that the compound consists of a polymer.

22. A composition as in Claim 21, characterized by the fact that the compound consists of a pH-sensitive polymer that consists of at least one repeating unit that has at least one basic function that is not a part of the backbone of the polymer.

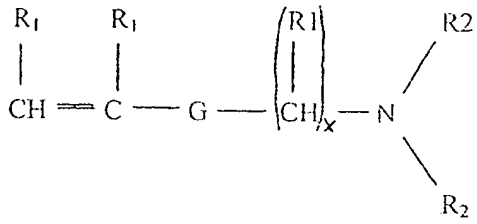
23. A composition as in Claim 22, characterized by the fact that the polymer consists of at least one repeating unit that is derived from a compound that is selected from the group that consists of polyvinyl alcohol derivatives, acrylates or alkyl acrylates that contain said basic function.

24. A composition as in Claim 22, characterized by the fact that the polymer is a carbohydrate that is functionalized with said basic function.

25. A composition as in one of Claims 22-24, characterized by the fact that the basic function is an amine.

26. A composition as in Claim 25, characterized by the fact that the basic function is a secondary or tertiary amine.

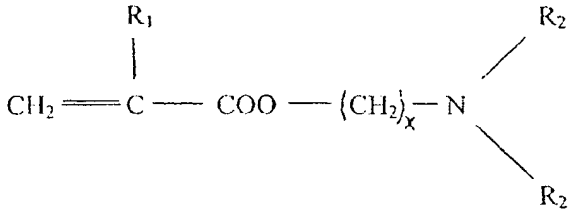
27. A composition as in Claim 26, characterized by the fact that the repeating unit is derived from a compound of the following formula III:



(III)

where G is a linking group that is selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, -NHCOO-, -OCONH- or -OCOO-, R_1, independent of one another, is hydrogen or an alkyl group with 1-3 carbon atoms, R_2, independent of one another, is hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1 to 6.

28. A composition as in Claim 27, characterized by the fact that the repeating unit is derived from a compound with the following formula IV:



(IV)

where R_1, independent of one another, is hydrogen or an alkyl group with 1-3 carbon atoms, R_2, independent of one another, is hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1 to 6.

29. A composition as in one of Claims 22-24, characterized by the fact that the basic function is an imine.

30. A composition as in one of Claims 22-24, characterized by the fact that the basic function is a basic aromatic N-containing group.

31. A composition as in Claim 30, characterized by the fact that the basic function is a pyridine group.

32. A composition as in Claim 30, characterized by the fact that the basic function is an imidazole group.

33. A composition as in Claim 24, characterized by the fact that the pH-sensitive polymer is a polymer that is derived from chitosan.

34. A composition as in Claim 18, characterized by the fact that the compound consists of κ-carrageenan.

35. A composition as in one of the preceding claims, characterized by the fact that the core(s) consist(s) of at least one material that is chosen from the group that consists of

surfactants, antibacterial compositions, antitarnish agents for silver, fragrances, bleaches, disinfection agents, agents to mask odor, antideposition agents and enzymes.

36. A composition as in Claim 35, characterized by the fact that the core (8;8') or at least a part of the cores (8") is in the form of an encapsulated liquid.

37. A composition as in Claim 36, characterized by the fact that the core (8;8') or at least a part of the cores (8") is in the form of a liquid contained in a gelatin capsule.

38. A composition as in Claim 35, characterized by the fact that the core (8;8') or at least a part of the cores (8") is in solid form.

39. A composition as in Claim 38, characterized by the fact that the core (8;8') or at least a part of the cores has a melting point of higher than 35°C.

40. A composition as in Claim 39, characterized by the fact that the core (8;8') or at least a part of the cores (8") has a melting point between 55 and 70°C.

41. A method for conducting a dishwashing cycle in a dishwashing machine, characterized by the fact that a composition as in one of Claims 1-40 is added to the medium in the dishwashing machine at a suitable time during the prerinse cycle or the main wash cycle.

42. A method as in Claim 41, characterized by the fact that, for the case that the base composition in the form of a tablet, after it has dissolved in the medium, is not capable of making available a concentration of the specific ion in the medium, before the end of the main wash cycle, that is sufficient to prevent significant dissolution of the coating and significant separation of the coating from the core, this sufficient concentration of the specific ion is made available through the addition of another composition, for example, a machine dishwashing agent composition, to the medium of the main wash cycle at a suitable time point.

[Key to previous page:]

1 pH profile
2 Time t (min)

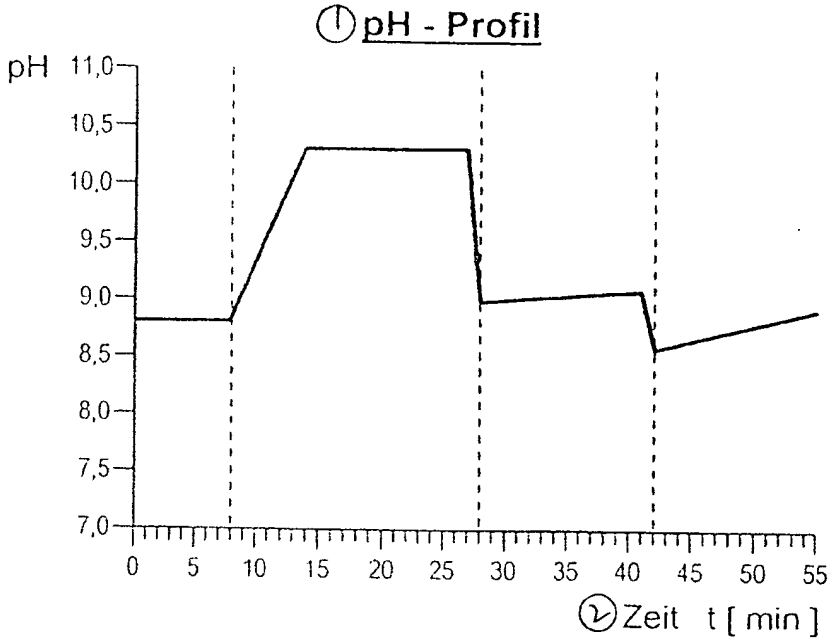

pH - Profil
pH
11,0
10,5
10,0
9,5
9,0
8,5
8,0
7,5
7,0
0
5
10
15
20
25
30
35
40
45
50
55
Zeit t [min]

Fig. 1

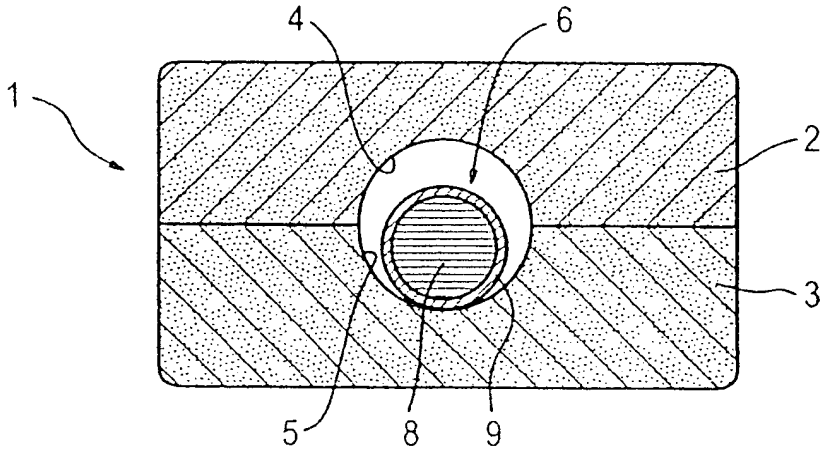


Fig. 2

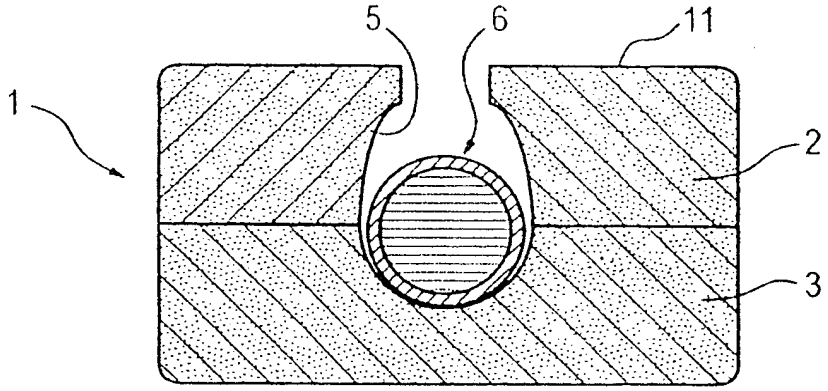


Fig. 3

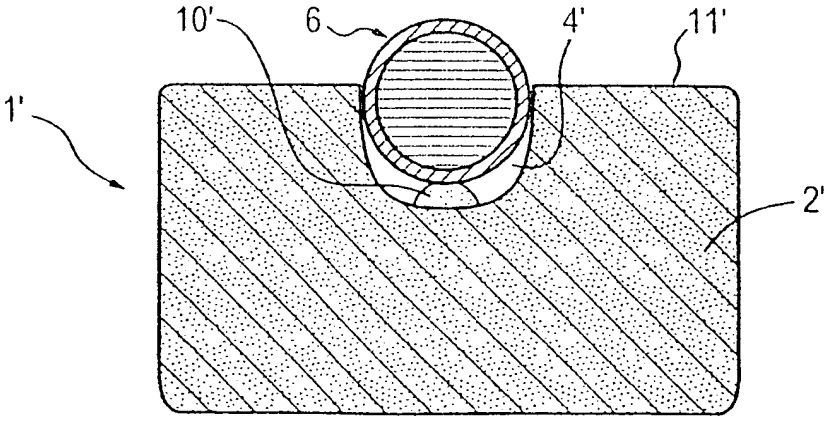


Fig. 4

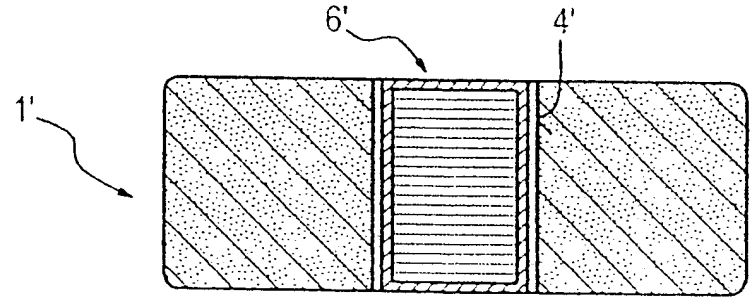


Fig. 5a

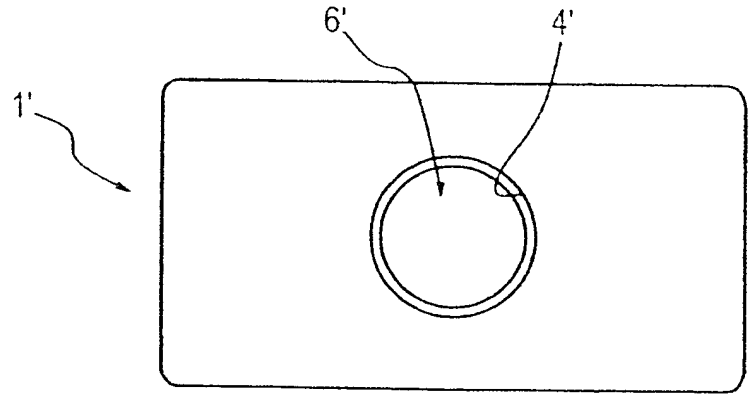


Fig. 5b

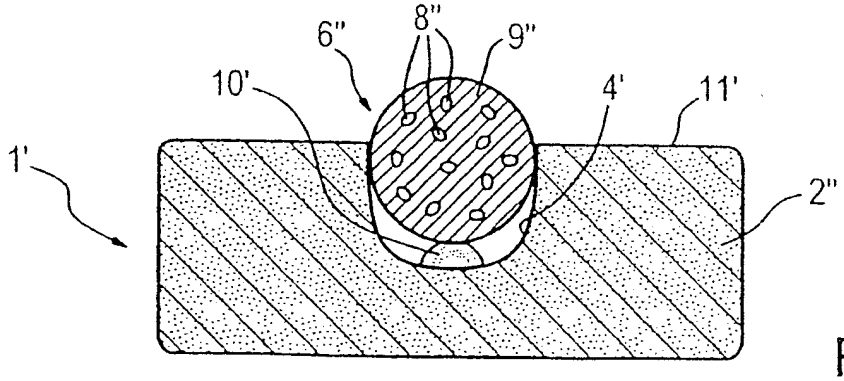


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 99/05265

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C11D 17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9927067 A1 (THE PROCTER & GAMBLE COMPANY), 3 June 1999 (03.06.99)	1-42
A	EP 0481547 A1 (UNILEVER PLC), 22 April 1992 (22.04.92)	1-42
A	WO 9927068 A1 (THE PROCTER & GAMBLE COMPANY), 3 June 1999 (03.06.99)	1-42

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 November 1999 (02.11.99)	13 December 1999 (13.12.99)
Name and mailing address of the ISA/	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/09/99

International application No.
PCT/EP-99/05265

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9927067 A1	03/06/99	NONE	
EP 0481547 A1	22/04/92	CA 2053399 A	18/04/92
		US 5133892 A	28/07/92
WO 9927068 A1	03/06/99	NONE	